

IV.A.1g Preparation and Reactions of Complex Hydrides for Hydrogen Storage: Metal Borohydrides and Aluminum Hydrides

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Objectives

ORNL is conducting research to develop the chemistry for a reversible hydrogen storage system based on complex hydrides, chosen mostly from the borohydrides, amides/imides, alane or the alanates of the light elements in the periodic table that will achieve the DOE/FreedomCAR performance targets for 2010.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Chemisorption and Physisorption

Technical Targets

ORNL is investigating high wt% materials, and efforts are directed toward making the release and uptake of hydrogen reversible. Percentages in Table 1 are for H₂ release only.

TABLE 1. Progress towards Meeting Technical Targets for Reversible Hydrogen Storage

Characteristic	Units	2010/2015 Targets	ORNL Status (System)
System Gravimetric Capacity	wt% (kg H ₂ /kg system x 100)	6%/9%	14.5% [Al(BH ₄) ₃]
			9.0% [Mg(BH ₄) ₂]
			11.4% [LiBH ₄ /Mg(BH ₄) ₂]

Accomplishments

Progress was made toward understanding the mechanism of hydrogen release from metal borohydrides.

- Completed study of temperature dependence of H₂/B₂H₆ ratio during decomposition of Al(BH₄)₃.
- Observed B₂H₆ as a decomposition product of alkali metal borohydrides and postulated mechanism of decomposition reaction.
- Eutectic mixture of LiBH₄ and Mg(BH₄)₂ decomposes at approximately the same temperature than either single salt, and absence of strong catalysis lends support to general decomposition mechanism involving MBH₄ going to MH and BH₃ in the first step.
- Prepared aluminoborane, AlB₄H₁₁, and observed low decomposition temperature (150°C).



Introduction

The focus of work at ORNL is the development of new materials, synthetic methods for materials, and studies of chemical reactions and processes that will lead to materials that will achieve the DOE/FreedomCAR performance targets for 2010. ORNL generally develops synthetic methods based on solution chemistry since these methods offer the most potential for scaling to kilogram and greater lot size. Synthetic methods are being developed and reactions are being studied for two types of target materials for hydrogen storage: complex anionic materials (Metal Hydride Center of Excellence [MHCoe] Project B) and amide/imide (M-N-H) systems (MHCoe Project C). For both types of materials ORNL is seeking (a) methods to scale-up synthesis of known materials or new materials identified by MHCoe

partners (b) development of new materials. ORNL is also collaborating with scientists at Brookhaven National Laboratory in MHCoE Project D, the alane focus group, with an emphasis on using the methods of solution inorganic and organo-metallic chemistry in an effort to regenerate alane.

Approach

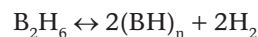
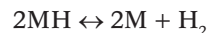
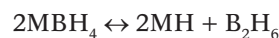
Our research involves materials from both known synthesis as well as those from newly designed synthetic procedures. The primary method used to follow the progress of reactions which release hydrogen is by temperature programmed pressure measurements where gaseous reaction products other than hydrogen are analyzed using a mass spectrometer or by infrared spectroscopy. Hydrogen uptake is investigated in a traditional Sieverts apparatus. Fourier transform infrared spectroscopy and X-ray diffraction (XRD) as well as solution nuclear magnetic resonance (NMR) are available at ORNL to characterize solid reaction products, and Raman and solid NMR are available through collaboration with MHCoE partners. Each material examined will initially be involved in a dehydrogenization study. Those materials found to be suitable hydrogen storage material candidates will then be examined for regenerative (hydrogen absorption) capability. From these results, chemical (and-or procedural) adjustment to the most promising of the materials will be made in order to obtain the optimal in hydrogen de/absorption capacity.

Results

The bulk of the research conducted during this review period was related to MHCoE Project B – Complex Anionic Materials, with this most recent study concentrated on the H_2 desorption mechanism of several metal borohydride materials. We had previously reported that the $Al(BH_4)_3$ system followed a temperature dependant product distribution that revealed a step-wise loss of diborane during the material's thermal H_2 desorption [1]. We sought to compare and contrast these results with those found with the other metal borohydrides. Of particular interests were those materials of $LiBH_4$, $NaBH_4$, and $Mg(BH_4)_2$.

Close observations of the $LiBH_4$ and $NaBH_4$ systems have shown that both of these materials slightly sublime and then melt prior to H_2 desorption. Mass spectroscopy analysis of the desorption gasses have also revealed the presence of trace amounts of diborane. An independent study of $LiBH_4$ has also reported the emission of diborane during its thermal desorption [2]. Powder XRD analysis of the residue at various stages of the desorption of each material has indicated the presence of the intermediate metal hydride and the final appearance of

elemental sodium. The much lighter lithium metal could not be detected by our XRD analysis. Nevertheless, our collective findings indicated that these two materials followed desorption mechanism similar to that of the $Al(BH_4)_3$ system as follows:



Although it is clear that both materials would exhibit diborane decomposition to form an amount of the hydrogen produced, we only have solid evidence that NaH also undergoes decomposition to form metallic sodium and hydrogen, while the results of the LiH species remains undetermined at this time. Further evidence of the resulting residue containing a $(BH)_n$ species instead of elemental boron is supported by findings of MHCoE partners in an article by Hwang et al., in which was revealed the existence of a $M(B_{12}H_{12})$ compound forming in the desorbed metal borohydride residue [3].

Our observation of the $Mg(BH_4)_2$ material's H_2 desorption has produced both striking similarities as well as profound differences compared to the other metal borohydrides in this study. Although this material exhibits a slight amount of sublimation and appears to go through a step-wise desorption process, the bulk of the material remains in the solid-state throughout the complete desorption process.

The desorption profile shown in Figure 1 reveals two distinct steps in the materials desorption. The first step, at $\sim 310^\circ C$ and 3.7 wt% hydrogen, corresponds to the loss of the first BH_3 unit, while the second step, at $\sim 340^\circ C$ and 7.4 wt% hydrogen, corresponds to the loss of the second BH_3 unit. In both instances, the BH_3 units are released as diborane of which would undergo a rapid thermal decomposition at such high temperatures.

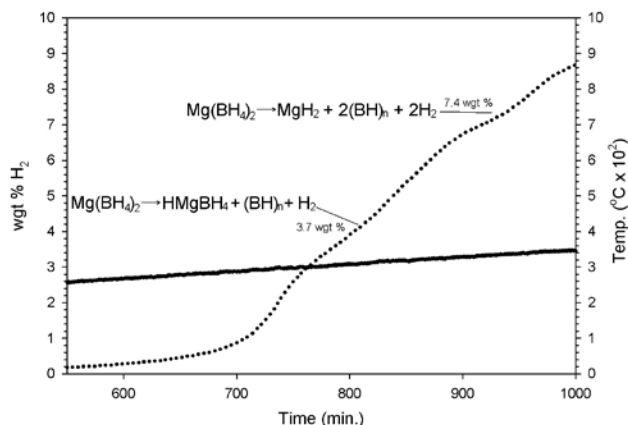
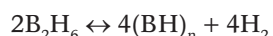
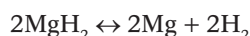
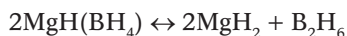


FIGURE 1. H_2 Desorption of $Mg(BH_4)_2$

Further evidence was obtained through a step-wise analysis of the powder X-ray diffraction (PXRD). Figure 2 shows PXRD patterns of the $\text{Mg}(\text{BH}_4)_2$ starting material as well as patterns of the residue at 295, 315, and 350°C. These patterns indicate how the material transforms into an amorphous unknown then into crystalline MgH_2 of which then transforms into magnesium metal at the end of the desorption. With this last piece of evidence we conclude that the $\text{Mg}(\text{BH}_4)_2$ material follows yet another, step-wise desorption process as did the other metal borohydrides as follows:



Although the MgH_2 , Mg metal, and $(\text{BH})_n$ (as the $\text{B}_{12}\text{H}_{12}^{+2}$ anion) components of this mechanism have all been identified [3], the hydridomagnesium borohydride, $\text{MgH}(\text{BH}_4)$ remains elusive and may be hidden in the amorphous material examined by PXRD at 295°C. There are only a couple of reports known that indicate this intermediate is fairly unstable and tends to disassociate into $\text{Mg}(\text{BH}_4)_2$ and MgH_2 under solvated conditions [4].

One important difference with the $\text{Mg}(\text{BH}_4)_2$ H_2 desorption is that under no circumstances (using similar desorption methods as with the other metal borohydrides) was any diborane, even at the slightest trace level, detected in the gasses evolved. Although all our other evidence points to this material undergoing a step-wise loss of diborane, no direct evidence of the existence of this diborane could be obtained. We surmise that this could be either a result of a completely solid-state absorption process, of which the diborane is simply trapped within a solid matrix before being

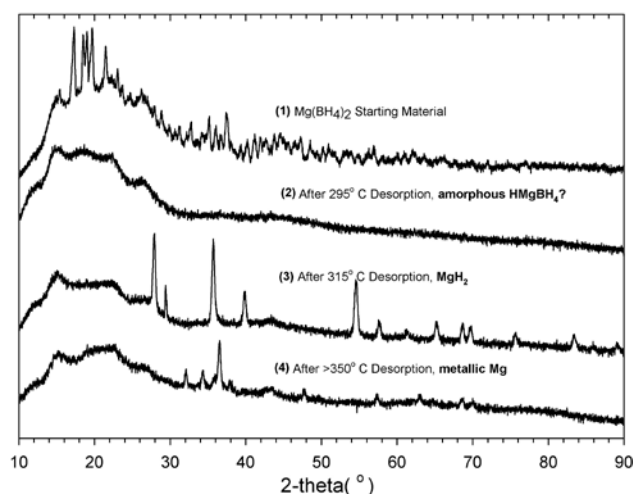


FIGURE 2. Step-Wise Powder X-ray Diffraction of the $\text{Mg}(\text{BH}_4)_2$ and Resulting Desorption Residue

decomposed, or the instability of the intermediate $\text{MgH}(\text{BH}_4)$ previously reported might have additional unknown chemistry that might involve and hold the released BH_3 species in a yet to be known fashion. In any case, this absence of detectable diborane is apparently unique to the $\text{Mg}(\text{BH}_4)_2$ system.

Attempts to synthesize bimetal borohydride systems has revealed an apparent *eutectic* effect as was found that a mixture of LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ would melt at $\sim 195^\circ\text{C}$. This type of eutectic effect was actually reported several years prior to this study using a 45:45:10 combination of LiBH_4 : KBH_4 : NaBH_4 of which apparently melted at $\sim 95^\circ\text{C}$ [5].

Unfortunately, although the LiBH_4 : $\text{Mg}(\text{BH}_4)_2$ *eutectic* melts at 100° less than the LiBH_4 , it was found that there was no significant effect on the finally desorption temperatures. The actual H_2 desorption temperatures were fairly similar to those found with the individual metal borohydrides. In fact, the data is indicating that each metal borohydride appears to desorb independently, even when brought together into a common melt.

Figure 3 presents a sample of the results obtained while observing the H_2 desorption of the LiBH_4 : $\text{Mg}(\text{BH}_4)_2$ *eutectic* alone and with a variety of titanium compounds as catalyst. The ration of each eutectic mixture was as the LiBH_4 / $\text{Mg}(\text{BH}_4)_2$ weight ratio, with the 0.82 ration as the most ideal eutectic mixture for these materials. As is shown, there is little effect to the H_2 desorption for each catalytic addition. Absorption was attempted (at 100 bar H_2 and up to 400°C), resulting in, at best, a 3 wt%

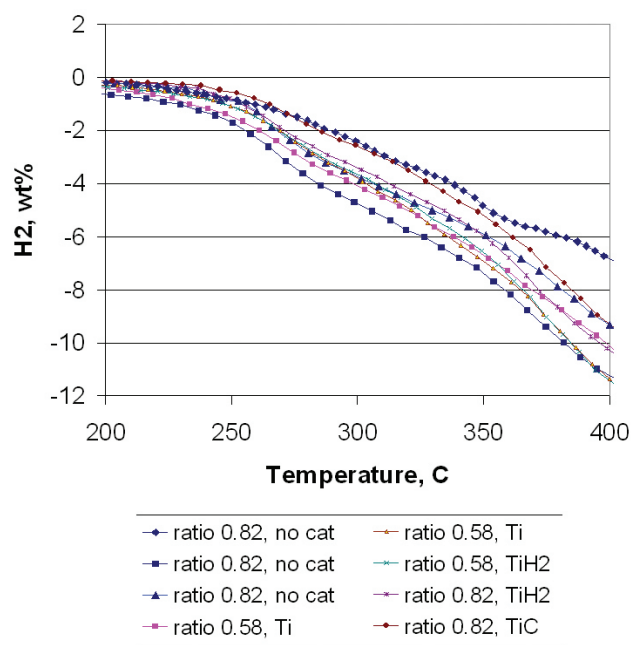


FIGURE 3. LiBH_4 - $\text{Mg}(\text{BH}_4)_2$, Typically 119 mg-69 mg Desorption, Ramp Rate $\sim 30^\circ\text{C/hr}$

H₂ absorption with no evidence of metal borohydride reformation at this time.

We are also studying the concept of hindered acid-base pairs as potential catalysts for the regeneration of alane. A system consisting of a long alkane chain hindered amine-tetrahydroalane solvent-electrolyte might be sufficiently stable and have close to the required weight percent hydrogen for an in situ system. Ionic liquids promote charge separation in reactions and we have prepared an ionic liquid composed of an organic cation and the tetrahydroaluminate anion. We prepared 1,2-dimethyl-3-butylimidazolium tetrahydroaluminate salt by reacting the corresponding imidazolium bromide with LiAlH₄ in acetonitrile, and the LiBr precipitate was removed by filtration. The reaction of this material with alane to form oligomeric alanate anions is being studied by solution NMR.

Conclusions and Future Directions

We will continue to investigate reactions and synthesize new and previously identified metal borohydrides. Of considerable interest are those compounds formed from the reaction of Al(BH₄)₃ with either diborane, forming AlB₄H₁₁, or ammonia, forming a possible Al(BH₄)₃-NH₃ material with the results of these studies to be presented in future reports. Further studies will also be performed in the eutectic systems beginning to be identified. One main objective is to find a suitable catalyst that will enhance both the desorption and absorption of hydrogen in these material systems. In addition to this, we will endeavor to build on the collection of known borohydride materials. As time permits we will begin investigating the chemistry of Ti(BH₄)₃ as well. This will allow us to test Ti and Ti-Al catalysis of decomposition reaction of metal borohydrides such as Al(BH₄)₃ and to determine whether catalysis helps to make the reaction reversible. The preparation of the known solid compounds LiM(BH₄)₄ where M = Al, Ti is accomplished by reaction of M(BH₄)₃ with LiBH₄ in solution, and the thermal decomposition reactions to make hydrogen and possible reversibility will be tested. We will attempt the preparation of Ca[M(BH₄)₄]₂ and Mg[M(BH₄)₄]₂ where M is Al, Ti by reaction of the alkali earth borohydride with Al(BH₄)₃ in a solvent. We will study the thermal decomposition reactions of these compounds; and determine reversibility of the hydrogen evolution. In the alane project we will continue to investigate ionic liquids as a reaction medium for alane regeneration using imidazolium and quaternary ammonium tetrahydroaluminates, the use of hindered amines to stabilize alane formation, and the use of alternative transition metal catalysts.

FY 2008 Publications/Presentations

1. "Complex Hydrides for Hydrogen Storage: Studies of the Al(BH₄)₃ System," Gilbert M. Brown, Douglas A. Knight, Joachim H. Schneibel, Ralph H. Ilgner, and Robert M. Smithwick, III Poster Presented at the DOE 2007 Hydrogen Annual Review, Washington, D.C., May 15-18, 2007.
2. "Metal borohydrides as hydrogen storage materials: The study of the thermal decomposition of Al(BH₄)₃," Douglas A. Knight, Gilbert M. Brown, Ralph H. Ilgner, and Robert M. Smithwick, III, Paper presented at the ACS National Meeting, Boston, MA, August 19, 2007.
3. "Investigation of the Thermal Desorption Mechanism of Several Complex Metal Borohydrides Towards the Development of Novel Hydrogen Storage Materials" An oral presentation at the Spring 2008 meeting of the Materials Research Society in San Francisco, CA, March, 2008.

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